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Laboratory evidence for volume-dominated nucleation of ice in supercooled water microdroplets

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Abstract

We report on measurements of the rate of homogeneous ice nucleation in supercooled water microdroplets levitated in an electrodynamic balance. By comparison of the freezing probability for droplets of radius 49 μm and 19 μm, we are able to conclude that homogeneous freezing is a volume-proportional process and that surface nucleation might only be important, if at all, for much smaller droplets.

1. Introduction

It is well known that supercooled liquid cloud and fog droplets are often encountered in the atmosphere at temperatures far below their equilibrium melting temperature and sometimes even below the frost point (Sassen and Dodd, 1988; Heymsfield and Sabin, 1989; Heymsfield and Miloshevich, 1993). Freezing phase transitions in such droplets play a crucial role in cloud microphysics, including the formation of lightning and precipitation (Pruppacher and Klett, 1998). While most of the atmospheric freezing processes occur heterogeneously via ice nuclei, homogeneous ice nucleation has been identified as important in the glaciation of thunderstorm clouds and the formation of high altitude cirrus clouds and polar stratospheric clouds. It forms the ultimate limit for supercooling. For a quantitative description of homogeneous nucleation, classical nucleation theory is usually invoked (Volmer and Weber, 1925; Zeldovich, 1942; Kelton, 1991). It is assumed that the formation of a single ice crystallite of a certain size (a germ or nucleus) initiates the crystallization of the whole droplet. The freezing process is then governed by a first order rate equation:

$$dP_u(t)/dt = -P_u(t) \cdot J(T) \cdot V \quad (1)$$

Here $P_u(t)$ is the probability for the droplet to be still unfrozen at time t after being quenched at time t=0 from high temperature to the temperature T. The freezing probability is proportional to the droplet volume and the proportionality constant $J(T)$ is

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called the (volume-) nucleation rate. Experimentally one usually measures ln ($P_u(t)$) as a function of time. If V and T are constant, this should yield a linear decline, the negative slope of which is then $J(T) \cdot V$. Nucleation rates of water ice have been measured previously by Taborek (1985) using emulsion samples, by DeMott and Rogers (1990) in cloud chambers, by Wood et al. (2002) in droplet trains and in levitated single particles by (Krämer et al., 1996; Krämer et al., 1999; Stöckel et al., 2002). In all cases the data were converted into a volume-nucleation rate.

There have been recent arguments by (Tabazadeh et al., 2002a, b; Djikaev et al., 2002; Djikaev et al., 2003) however, that surface nucleation might be dominant under atmospheric conditions. In principle, the free enthalpy of nucleation on the surface is different from the volume value. If it is smaller, then surface nucleation is favored and the ratio of the numbers of surface-to-volume-nucleation sites determines the role of surface nucleation under atmospheric conditions (c.f. below). Dominant surface nucleation would have important consequences, as the surface of cloud and aerosol particles is much more prone to anthropogenic and natural modification than the volume material.

In order to include surface freezing, Eq. (1) should be replaced by the more precise form

$$dP_u(t)/dt = -P_u(t)[J_V(T) \cdot V_V + J_S(T) \cdot V_S], \quad (2)$$

where V_V is the bulk volume, J_V is the volume nucleation rate, V_S is the surface volume, i.e. the volume of the surface layer that is governed by surface freezing and J_S is the surface nucleation rate. If, for simplicity, we assume spherical symmetry and $V_V \gg V_S$ we can bring this into the form:

$$dP_u/dt = -P_u(t) \cdot J_V \cdot V \cdot \left(1 + \frac{1}{r} \cdot \frac{3d_s \cdot J_S}{J_V}\right) = -P_u(t) \cdot J_V \cdot V \cdot \left(1 + \frac{r_c}{r}\right) \quad (3)$$

Here d_S is the thickness of the surface layer and r is the radius of the droplet. The correction due to surface nucleation is given by the second addend in the brackets

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and is inversely proportional to the droplet radius r. The proportionality constant $r_c = 3 d_S J_S / J_V$ has the dimension of a length and can be interpreted as the critical radius of a droplet, for which surface- and volume-nucleation are equally important. For larger droplets volume nucleation prevails and vice versa. In order to assess the role of surface nucleation in atmospheric processes, the typical droplet size of interest has to be compared to r_c.

Fortunately, r_c can be determined directly by experiment. It is sufficient to measure α, the ratio of the freezing probabilities of two different monodisperse droplet ensembles of radii r_1 and r_2 respectively compared to the volume ratio of the two ensembles:

$$\alpha = \frac{V_1}{V_2} \cdot \frac{J_V(T) \cdot V_{V2} + J_S(T) \cdot V_{S2}}{J_V(T) \cdot V_{V1} + J_S(T) \cdot V_{S1}} = \frac{(1 + r_c/r_2)}{(1 + r_c/r_1)} \quad \text{or} \quad r_c = \frac{\alpha - 1}{1/r_2 - \alpha/r_1} \tag{4}$$

Here we report on such a measurement performed for droplets of radius $r_1 = 49\,\mu$m and $r_2 = 19\,\mu$m at a temperature of 237.1 K corresponding to a supercooling of 36.1 K.

2. Experimental

The freezing of about hundred individual droplets of each size was observed inside an electrodynamic levitator which was kept at the low temperature of interest throughout the experiment. The method of electrodynamical levitation was reviewed by Davis (1997), details of our experimental setup have been given elsewhere (Duft et al., 2002; Duft and Leisner, 2004). Briefly, the levitator is of hyperboloidal type as proposed for microparticles by Fischer (1959) and Wuerker and Langmuir (1959) consisting of a rotationally symmetric torus electrode and two endcap electrodes (c.f. Fig. 1a, b, c). The central torus electrode is formed to serve as a climate chamber and carries various ports for optical access to the droplets. It also embodies two linear CCD (charge coupled device) array detectors (Fig. 1d) to measure the angular resolved intensity of light scattered by the droplet from a HeNe laser beam (phase function measurement). As Duft and Leisner (2004) have shown recently, the analysis of the phase

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function allows to determine the size and refractive index of the droplets in real time. The trap setup is housed inside a vacuum chamber (Fig. 1f) for thermal insulation and connected to a liquid nitrogen cooled micro- cryostat for temperature adjustment. Great care has been taken to guarantee temperature uniformity over the trap volume.

The two size classes of droplets of different diameter were generated and injected into the levitator by a piezoelectric droplet on demand generator (Fig. 1e) which was operated at room temperature at two different driving pulse amplitudes. The droplets of the first class (low driving pulse amplitude) had a diameter d_1=98±1 μm while the droplets of class two are straggler droplets which occur at high driving pulse amplitude and were characterized by a size of d_2=38±0.5 μm. In order to be levitated electrodynamically, each droplet carries a specific charge of about 10^{-4} C/kg. In the case of the larger droplets, this corresponds to roughly 10^6 additional H_3O^+ ions distributed homogeneously around the surface, which is made up by about $1.5{\cdot}10^{11}$ molecules. These numbers indicate that there are plenty of undisturbed sites available for surface nucleation. In previous experiments by Krämer et al. (1999), the surface charge was varied by a factor of three and no detectable influence on the rate of homogeneous freezing was found for both positively and negatively charged droplets.

Freezing phase transitions in droplets can easily be detected by light scattering measurements. The phase function of a liquid droplet shows well resolved intensity minima and maxima as expected from Mie theory for a homogeneous sphere, while the frozen ice particles generate a highly irregular light scattering pattern due to multiple scattering on the grain boundary network. An automated phase function analysis is used to determine the time of freezing for each droplet with a time resolution of 10 ms. The freezing probability of the droplets is determined by plotting the logarithm of the frequency of occurrence of unfrozen droplets versus the time after injection. The results for both size classes are given for a temperature of T=237.1 K in Fig. 2.

The data do not lie exactly on a straight line as expected both from Eqs. (2) and (3) but rather start off with a horizontal slope. This is especially evident in Fig. 2a and reflects the fact that the droplets are injected into the levitator at room temperature and

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then have to accommodate to the trap temperature. After this thermalization, which takes longer time for larger droplets, the curves assume a constant slope. From this slope, freezing probability is deduced for both sizes. For increased accuracy, this is done by fitting a solution to a differential equation, which takes the initial cooling period into account. Details of this analysis will be given in a subsequent publication. The fitted curve in Fig. 2b may seem to be too flat, this is due to the fact that in Fig. 2b data points at longer times (t>15 s) are omitted for clarity. These data points have been taken into account in the fitting procedure. The result of the measurements is summarized in Table 1.

3. Discussion

If we interpret our data in the framework of volume freezing, we arrive at a freezing rate $J_V = (2.8 \pm 0.15) \cdot 10^6\ \mathrm{cm}^{-3}\ \mathrm{s}^{-1}$, a value which is in very good agreement with previous measurements. Comparing the two size classes, we find that the volume ratio V_1/V_2 and the freezing probability ratio lie within the limits of error of each other. Accordingly, the volume nucleation rates in the two classes are equivalent. If, for comparison, we convert our results to surface nucleation rates, the resulting rates are about a factor of 2.5 apart for the two size classes. We conclude that within the investigated size range, the freezing probability of supercooled water scales with the droplet volume and therefore is a volume process. Surface freezing is not needed to explain the results. If we want to stress our data somewhat, we can determine the droplet radius below which surface nucleation becomes important. With the help of Eq. (4) we find a critical radius of $r_c = 1\ \mu\mathrm{m}$. It has to be noted however, that this critical radius carries a large error bar, any value between $r_c = 0$ and $r_c = 4\ \mu\mathrm{m}$ is consistent with our data.

Our results suggest that for droplet radii of some ten micrometers, as they are commonly encountered in tropospheric clouds, homogeneous nucleation proceeds by a volume proportional rate. It cannot be ruled out however, that surface nucleation is important for much smaller droplets below 1 μm, as they are typical for aerosol droplets.

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The main argument that supported surface nucleation was based on laboratory measurements from various groups which yielded varying volume- nucleation rates. These experimental data seemed more consistent if interpreted as surface nucleation rates. In the light of our results we rather assume that the differences in nucleation rate measurements were related to experimental problems with the assessment of droplet volume and temperature instead. This has been confirmed for the data presented by Stöckel et al. (2002). Revised and extended data by Stöckel et al. (submitted, 2004)[1] support this point of view.

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Table 1. Comparison of the freezing probabilities of water droplets of different size.

Temperature T=237.1 K	Size class 1	Size class 2	Ratio (class1/class2)
Radius (μm)	49±0.5	19±0.25	2.58±0.05
Volume (μm^3)	$(4.93\pm0.15)\cdot10^5$	$(2.87\pm0.1)\cdot10^4$	17.2±0.8
Freezing probability (s^{-1})	1.35±0.05	$(8.2\pm0.3)\cdot10^{-2}$	16.5±0.6
Volume nucleation rate ($cm^{-3}s^{-1}$)	$(2.75\pm0.15)\cdot10^6$	$(2.85\pm0.15)\cdot10^6$	0.96±0.07
Surface nucleation rate ($cm^{-2}s^{-1}$)	$(4.47\pm0.19)\cdot10^3$	$(1.81\pm0.075)\cdot10^3$	2.47±0.15

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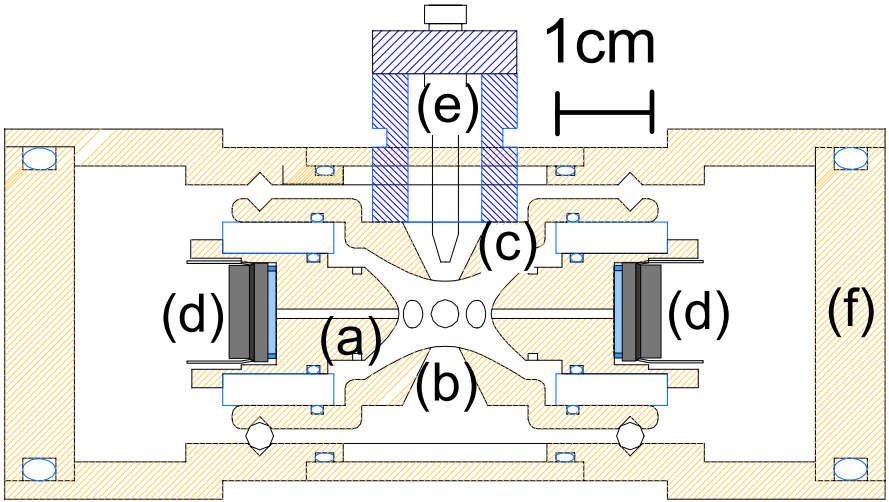

Fig. 1. Schematic vertical cross section through the levitator, **(a)** cooled central electrode, **(b)** bottom and **(c)** top endcap electrode, **(d)** linear CCD detectors, **(e)** droplet generator and injector, **(f)** vacuum chamber.

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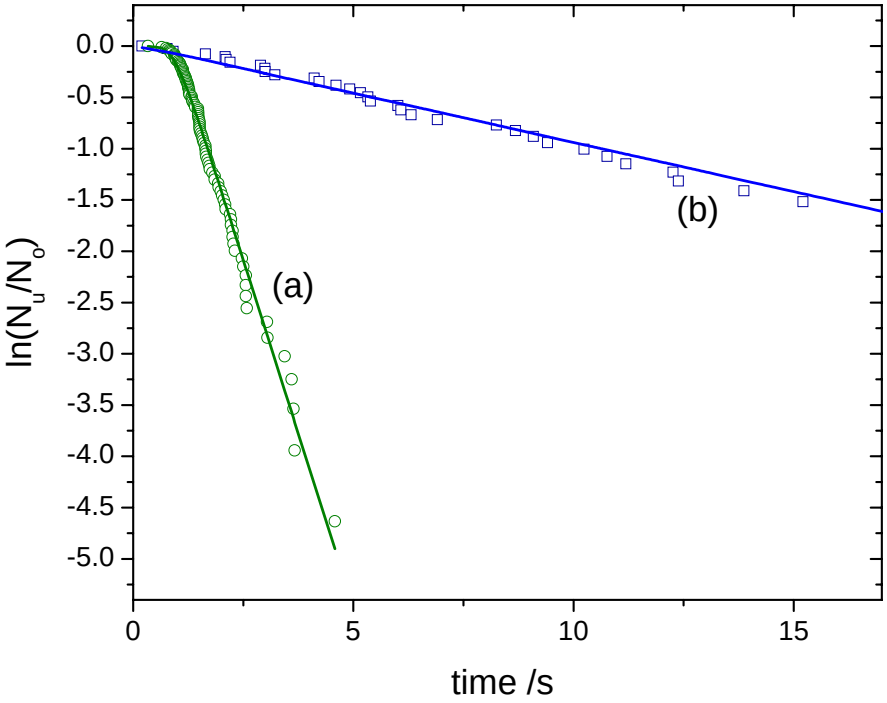

Fig. 2. Logarithm of the fraction of unfrozen droplets as a function of time after injection in the droplet levitator. **(a)** open circles: large droplets with an average radius r_1=49 μm, **(b)** open squares: small droplets with an average radius r_2=19 μm.

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